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**FORMATION OF ALKALI IRON SULFATES
AND OTHER COMPOUNDS CAUSING CORROSION
IN BOILERS AND GAS TURBINES**

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PROJECT REVIEW

July 1, 1966 - June 30, 1968

AND

FOURTH SUMMARY REPORT

January 1, 1968 - June 30, 1968

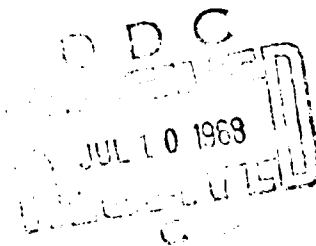
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AMERICAN SOCIETY OF MECHANICAL ENGINEERS

**Research Committee On Corrosion And
Deposits From Combustion Gases**

Prepared by
BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories



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FOREWORD

This Final Summary Report is in two parts, the first marked GENERAL REVIEW, and the second TECHNICAL DETAILS. The first part summarizes the most important findings over the past two years in this study of how compounds are formed that cause metal wastage. Those interested generally in how corrosion occurs in hot flue gas will find Battelle's major findings and conclusions listed here. The second part of this report is technically oriented and covers the experimental work done in the laboratory over the last six months of the study. This is the last report on this program, concluding six years of research on the fundamentals of external corrosion in combustion atmospheres under the sponsorship of the ASME Research Committee on Corrosion and Deposits from Combustion Gases.

PROJECT REVIEW AND FOURTH SUMMARY REPORT

on

FORMATION OF ALKALI IRON SULFATES
AND OTHER COMPOUNDS CAUSING CORROSION
IN BOILERS AND GAS TURBINES

to the

AMERICAN SOCIETY OF MECHANICAL ENGINEERS
RESEARCH COMMITTEE ON CORROSION AND
DEPOSITS FROM COMBUSTION GASES

July 1, 1966 - June 30, 1968

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The American Society of Mechanical Engineers

United Engineering Center / 345 E. 47th St., New York, N. Y. 10017 / 212-752-6800

July 8, 1968

ASME Research - Corrosion and Deposits From Combustion Gases

Enclosed is a copy of the Fourth Summary Report and Project Review of the study of "Formation of Alkali Iron Sulfates and Other Compounds Causing Corrosion in Boilers and Gas Turbines". This report covers in detail work performed at Battelle from January 1, 1968 through June 30, 1968, and reviews the work of the entire project between July 1, 1966 and June 30, 1968.

During the last six months, experiments were continued using radioactive sulfur which demonstrated the much greater reactivity of SO_3 relative to SO_2 with surfaces such as are present in a combustion gas stream. This was a continuation of work performed during the previous six months, and investigated the effects of lower SO_2 concentration, less oxygen, and varying the temperature of the surface. Further experiments were also made in a small fuel-burning furnace in which a newly-designed sample-holder was used to determine the SO_3 concentration beneath various compositions of deposits.

This is the final report on this project, as the work was terminated on June 30, 1968 because of financial limitations. It is believed that this work has contributed new knowledge toward understanding the reactions that lead to corrosion and deposit problems in combustion gases. The Committee sincerely appreciates your interest in this project, and the report is sent to you in recognition of your support of this research.

Very truly yours,

George C. Wiedersum, Chairman
ASME Research Committee on Corrosion
and Deposits From Combustion Gases

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Enclosure

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TABLE OF CONTENTS

	<u>Page</u>
GENERAL REVIEW	1
Scope of the Research	3
Research Accomplishments	4
Test and Analytical Techniques	4
Optical Identification of Trisulfates	4
Radioactive Tracing With S ³⁵	5
Electrochemical Indication of Corrosion	6
SO ₃ Gradient Over Catalytic Surfaces	6
Catalytic Activity of Fly Ash	8
Catalysis and Reactivity of Surfaces	9
Relative Reactivity of SO ₃ and SO ₂	10
SO ₃ Concentration Beneath Deposits	11
Trisulfates in Deposits From Operating Boiler Furnaces and Gas Turbines	12
The Future	13
Reports and Publications	15
 SURFACE INVESTIGATIONS	
Sulfur-35 Studies	17
Effect of Temperature	17
Effect of SO ₂ and O ₂ Concentration	19
Reactivity of Magnetic (Y) Fe ₂ O ₃	20
Reactivity of Fe ₃ O ₄	22
Identification of Compounds in Boiler Deposits	24
 FURNACE STUDIES	25
 CORROSION FROM SULFUR-CONTAINING COMPOUNDS	31
 LIST OF REFERENCES	34
 APPENDIX - List of Publications, 1962-1968	35

LIST OF TABLES

Table 1. Index of Refraction of Alkali Iron Trisulfates	4
Table 2. Comparative Catalytic Activity of Fly Ashes and Iron Oxide	3
Table 3. Reactivity of SO ₃ (30 ppm) and SO ₂ (5.8%) Toward Na ₂ SO ₄ -Fe ₂ O ₃ Mixture at Different Temperatures	18
Table 4. Effect of SO ₂ and O ₂ Concentration on Reactivity of SO ₂ and SO ₃	19

LIST OF FIGURES

	<u>Page</u>
Figure 1. Refractive Index of Alkali Iron Trisulfates	5
Figure 2. SO ₃ Gradient Over Surfaces	7
Figure 3. Effect of Flow Velocity on SO ₃ Gradient Above Fe ₂ O ₃	8
Figure 4. Rate of Conversion of Gamma-Fe ₂ O ₃ to Alpha-Fe ₂ O ₃ as a Function of Temperature	20
Figure 5. Effect of Type of Fe ₂ O ₃ on Reactivity of SO ₂ and SO ₃ With Na ₂ SO ₄ -Fe ₂ O ₃ Surface at 900 F	21
Figure 6. Reaction Sequences of Iron Oxides and Alkalies With Sulfur Oxides	22
Figure 7. Reactivity of SO ₂ and SO ₃ With Surfaces Containing Iron Oxides and Na ₂ SO ₄ at 1100 F	23
Figure 8. System for Determining Effect of Deposits on Formation of Corrosive Conditions in Fuel-Fired Furnace	25
Figure 9. SO ₃ Concentrations Above and Beneath Deposits	28-29
Figure 10. Effect of Temperature and SO ₃ Concentration on the K ₂ SO ₄ -K ₂ S ₂ O ₇ System	32

Project Review and Fourth Summary Report

on

FORMATION OF ALKALI IRON SULFATES

AND OTHER COMPOUNDS CAUSING CORROSION

IN BOILERS AND GAS TURBINES

Completion of the work with S^{35} as a tracer of reactions on surfaces has confirmed that SO_3 is hundreds of times more reactive than SO_2 . Variations in O_2 level and in temperature have only a minor effect on this reactivity ratio. Investigation of the formation of SO_3 beneath simulated deposits has shown that little SO_3 remains in the gas phase beneath mixtures of alkali sulfates and iron oxides when the complex trisulfates are being formed. Using the index-of-refraction technique, traces of trisulfates can be detected after as little as five hours' exposure to flue gas at 1100 F. Broad recommendations are made here to the Committee for a future study of practical means of preventing deposits.

GENERAL REVIEW

1966-1968

by

William T. Reid

When this study of the causes of metal wastage in boilers and gas turbines began in May, 1962, it was aimed mainly at learning more about the basic thermochemical reactions between the flue gas, the alkalies, sulfur, and vanadium in fuel ash, and the oxides on metal surfaces. Because complex sulfates had already been identified as an important contributor to high-temperature corrosion, and because SO_3 was necessary that these sulfates could form, much of the research early in this project was devoted to a detailed study of the formation of SO_3 in

flames. Part of those combustion studies was carried out under idealized laboratory conditions burning H_2S in a thin, stabilized flame; the other studies were made in a furnace burning sulfur-doped natural gas or No. 2 fuel oil. The tests in the fuel-burning furnace made it possible to relate the thin-flame studies to conditions more nearly representing those in full-scale systems such as boiler furnaces and gas turbines.

By means of these flame studies, the combustion reactions were identified that lead to SO_3 . The tests also showed the importance of reactions occurring on the oxidized surface of metals, where alkalies and the oxide films normally present on the metal can react with SO_3 . Also important was the finding that SO_3 resulting from homogeneous flame reactions would be insufficient to permit complex sulfates to form, and that only heterogeneous reactions on surfaces, either on the oxidized metal or in the deposit, seemed likely to lead to the required high concentrations of SO_3 . Out of this work came a confirmation that surface reactions could be extraordinarily complex, that predictions of the course of these reactions were uncertain, and that a logical description of the corrosion process would depend largely on knowing precisely what reactions occur on surfaces, the conditions that influence them, and the rate at which they take place.

Hence, in July, 1966, with flame-induced reactions now adequately covered, the project was re-oriented toward detailed studies of the formation of alkali iron trisulfates and other compounds causing corrosion. Again, the research was carried out in two main areas. One was directed solely to the reactions that occur on surfaces, using glass reaction systems and simulated flue gases. The other was carried out in the fuel-burning furnace, with specially designed specimens of various types exposed to actual furnace atmospheres. Together, these provide a good measure, for example, of the catalytic nature of various surfaces and how they are influenced by deposits and gas velocity; of the relative reactivity of SO_2 and SO_3 in forming complex sulfates; of methods of detecting corrosion conditions on surfaces; of means of identifying alkali iron trisulfates in extremely low concentrations, too minute to be found by X-ray diffraction; and of evaluating the changes in gas composition beneath deposits as compared with the bulk flue gas.

Over these past two years a great deal of information has been accumulated on these points. Despite this, corrosion still occurs on superheaters and in gas turbines, mainly because basic information on corrosion reactions cannot be applied as yet in the field, or there are good economic reasons for not changing plant practices. A gap still exists between the laboratory and the full-scale plant. For one thing, the sheer size of a modern boiler furnace poses problems in identifying the exact conditions that exist from point to point, coupled with inability to define even such basic parameters as temperature variations of a superheater tube with a swinging load and normal deslagging. The three major ways of combatting corrosion in superheaters, of limiting steam temperature to no more than 1000 F, of operating oil-fired equipment with essentially no excess air, and the use of additives in oil-fired boilers, are examples of practical engineering-type solutions to the problem. Hopefully, in the years ahead, the data in this report on the research at Battelle will lead to equally successful results with other methods of preventing metal wastage.

SCOPE OF THE RESEARCH

Much of the work reported in the literature on the direct causes of external corrosion assumes the presence of alkali iron trisulfates. In some laboratories, a corrosive environment has been provided by mixing alkali sulfates and iron oxide and then exposing the mixture to a nearly stagnant atmosphere containing SO_2 and O_2 to simulate flue gas. At temperatures between 1000 F and 1100 F, conditions are ideal for forming $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ and $\text{K}_3\text{Fe}(\text{SO}_4)_3$, as was noted in the early 1940's when these trisulfates were first synthesized and identified as the corrosive material in a boiler furnace. That these mixtures do indeed form highly corrosive products is no longer a matter of argument. The unanswered question is "how are they produced in a furnace?"

Earlier experiments did not identify the series of steps that must take place in forming the trisulfates by reaction between the flue-gas-borne alkalis and sulfur oxides and the iron oxides on tube surfaces and in fly ash. Equally important, they did not specify the effect of the many physical factors that must be involved, such as the thermal gradient through the deposit overlying the tube surface where the trisulfates can form, the nature of the stagnant gas film beneath a deposit, and the migration of gases and alkalis through the deposit to the cooler tube surface. These factors all affect the rate at which alkalis and sulfur oxides are transported to the tube surface, and how completely that surface is "ventilated" beneath a deposit. They also establish the residence time and the conditions under which SO_2 can be oxidized to SO_3 , leading to the possible production at the tube surface or in the deposit of an atmosphere rich enough in SO_3 that the trisulfates can form.

Hence, the scope of this two-year program was established as:

1. A study of the interactions between such solids as Fe, Fe_3O_4 , and Fe_2O_3 and such gases as O_2 , SO_2 , and SO_3 in the presence of alkalis and other ash constituents.
2. Investigation of the physical factors occurring within deposits that lead to the formation of trisulfates.

The first of these has been checked in detail, the second less completely. Chemical reactions on surfaces are now well understood, and there has been considerable information generated on the role of deposits. Nevertheless, there is great difficulty in the laboratory in synthesizing deposits with the same characteristics as those formed in boilers and gas turbines. Results reported here cover only a few of these variables. Hence, more elaborate studies with much more complicated experimental apparatus are still needed to establish exactly how changes in the physical and chemical properties of deposits affect corrosion conditions, or, more importantly, how deposits can be prevented in the first place.

RESEARCH ACCOMPLISHMENTS

Test and Analytical Techniques

Three procedures for following corrosion reactions were investigated these past two years, of which two were developed to the point where they can be considered reliable research tools:

- An optical method for identifying trisulfates can detect trace amounts of these compounds as an indication of incipient corrosion long before any appreciable metal wastage actually occurs.
- Radioactive S^{35} provides a useful method of following corrosion reactions whereby the source of the sulfur in a given reaction product can be positively identified.
- Electrochemical techniques for indicating the onset and extent of corrosion offer considerable promise, but the many variables that affect the output of electrochemical cells can lead to spurious results.

Optical Identification of Trisulfates

A major shortcoming of X-ray diffraction methods for detecting the presence of alkali iron trisulfates in suspected corrosion areas is that the sample must contain at least 10 percent of the trisulfate to permit positive identification. An optical method developed at Battelle based on the index of refraction of the trisulfates now permits identifying even single microscopically small crystals. For example, crystals of $Na_3Fe(SO_4)_3$ have been detected in a laboratory sample after only four hours exposure at 1100 F to an atmosphere containing SO_3 .

To develop this technique, pure samples of $Na_3Fe(SO_4)_3$ and $K_3Fe(SO_4)_3$ were prepared in the laboratory. The index of refraction of these pure compounds was then determined, using conventional microscope immersion procedures with standard, readily available index-of-refraction oils. Because these trisulfates form hexagonal crystals, two values of the index of refraction of each trisulfate were measured, one for each axis as shown in Table 1. Measurements of the index of refraction along two axes for each crystal assure good accuracy.

TABLE 1. INDEX OF REFRACTION OF
ALKALI IRON TRISULFATES

Compound	Index of Refraction	
	Long Axis	Short Axis
$Na_3Fe(SO_4)_3$	1.626	1.590
$K_3Fe(SO_4)_3$	1.622	1.584

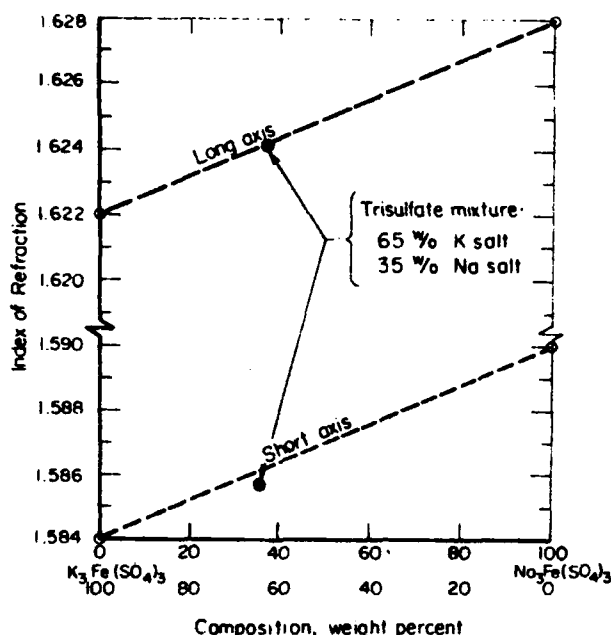


FIGURE 1. REFRACTIVE INDEX OF ALKALI IRON TRISULFATES

These trisulfates seldom occur separately. But fortunately, as solid solutions are formed with varying ratios of potassium to sodium, the index of refraction changes essentially linearly. Hence, measurements of the index of refraction also can identify the relative proportions of the potassium and the sodium salts in a mixed trisulfate. Figure 1 shows a typical case where a mixture containing 65 percent $\text{K}_3\text{Fe}(\text{SO}_4)_3$ and 35 percent $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ had indexes of refraction almost exactly in accordance with predicted values.

Any skilled microscopist can make such analyses, requiring only that oils of the proper index of refraction are available. Analysts can learn the technique easily.

Radioactive Tracing With S^{36}

Identifying which one of the oxides of sulfur causes corrosion can be difficult if both SO_2 and SO_3 are available, yet it is important to know which of these sulfur oxides is mainly responsible for metal wastage. Radioactive S^{36} , which can be incorporated in the gas mixture as a very small amount of S^{36}O_2 or S^{36}O_3 to label the corresponding normal oxides, permits measuring the corrosion attributed to either of these sulfur oxides by determining the radioactivity of the reaction products. Except for Fletcher and Gibson⁽¹⁾, who worked with S^{36} in England in 1954, such radioactive tracer techniques generally have been passed over in corrosion research.

Radioactive S^{36} emits low-energy beta radiation at 0.167 mev, and has a half-life of 86.7 days. It is relatively safe to handle in the laboratory, while its radioactive decay is rapid enough to give a significant radioactive count over reasonable time periods. As radioactive tracers go, S^{36} poses less problems than most isotopes.

Because the minimum amount of S^{36} that can be measured quantitatively is so small, this isotope need make up but a tiny fraction of the total gas mixture. In the tests here, there was 10^{10} times more nonradioactive sulfur than S^{36} . Yet, because the S^{36} behaves chemically exactly like ordinary sulfur, even this small quantity gives a precise measure of how all the sulfur is reacting.

As will be noted later, labelling SO_2 and SO_3 separately with S^{35} has permitted accurate measurements of the relative reactivities of these gases on surfaces. The technique should be equally useful in other corrosion studies where sulfur is a participant.

Electrochemical Indication of Corrosion

In searching for ways of detecting the onset of corrosion in short-term laboratory tests, several electrochemical cells were devised and evaluated. The simplest was a pair of dissimilar metal electrodes separated by a slight gap. When a molten electrolyte bridges that gap, as would be the case if alkali iron trisulfates were present at temperatures between 1000 F and 1200 F, a voltage should be produced indicating corrosion. In a test of the method with mild steel and stainless steel as the two electrodes, immersed in a mixture of Na_2SO_4 , K_2SO_4 , and Fe_2O_3 in an atmosphere containing SO_3 , no voltage was observed on heating until the temperature reached 1020 F. At that point, voltage was produced abruptly, almost exactly when a liquid phase should have formed. Further tests of the system showed it to be unreliable when heated and cooled many times, but as a one-shot indicator of corrosion it appears to have some merits.

More elaborate systems using platinum as one electrode and iron as the other have shown abrupt increases in voltage when trisulfates were being formed, but in some cases the voltage increased even when later microscopic examination showed no trisulfates present. In most tests, when corrosion could have been occurring, there was an abrupt increase in voltage each time the temperature was increased stepwise, followed by a gradual decrease in voltage as the cell was held at a constant temperature. Such behavior can be explained on the basis of formation of an oxide film on the iron electrode, but the exact mechanism is obscure. A relation possibly exists between formation of this oxide film and its eventual conversion to a trisulfate, but the extreme sensitivity of electrochemical systems to slight changes in conditions prevents drawing firm conclusions on the exact mechanism here.

Electrochemical corrosion indicators still appear promising for use in the field. However, considerable development will be necessary to provide an instrument that is more reliable and less confusing than those versions investigated in this study.

SO_3 Gradient Over Catalytic Surfaces

Because high SO_3 concentrations are necessary to form trisulfates, considerable work was done on the levels of SO_3 reached in gas mixtures flowing over catalytic surfaces. At low velocities, it was reasoned that although the bulk flue gas would contain only 30 ppm to 50 ppm of SO_3 from flame reactions, much higher concentrations might exist in the boundary layer if the surface were catalytic. Further, if this surface also were reactive toward SO_3 , conditions would be ideal for corrosion.

The test equipment was simple - an electrically heated glass tubular furnace with the surface being investigated mounted parallel to the gas flow at the center of the furnace. A needle-like gas-sampling probe with an orifice only 0.0011 inch in diameter (30 microns) perpendicular to this surface could be moved into various parts of the boundary layer. A cathetometer was used to measure the distance between probe and surface. The minimum distance that could be measured between the surface and the probe was about 0.005 inch, fixed mainly by irregularities in the surface roughness.

Figure 2 typifies the kinds of results obtained at 1100 F when the gas mixture nominally contained 75 percent N_2 , 19 percent O_2 , and 6 percent SO_2 . The volume flow rate of this gas mixture over the surface, which was deposited on inert Vycor glass to eliminate any effects from a substrate, was 40 cc per second for a flow velocity of 0.79 inch per second and a residence time of 1.3 seconds.

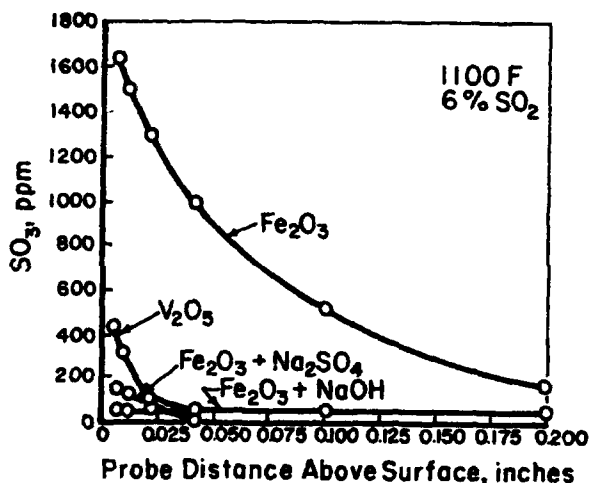


FIGURE 2. SO_3 GRADIENT OVER SURFACES

It is evident that Fe_2O_3 is extremely effective in increasing the SO_3 concentration near the surface. Within 0.005 inch of the Fe_2O_3 layer, the SO_2 concentration was more than 1600 ppm. Vanadium pentoxide is less effective, increasing the SO_3 at the same distance only to about 450 ppm; a commercial vanadium catalyst when crushed gave 650 ppm SO_3 .

Probably most significantly, when Na_2SO_4 was mixed with Fe_2O_3 , there was only a slight increase in SO_3 in the boundary layer, and when NaOH was present there was no SO_3 gradient. The probable explanation here is that these mixtures captured SO_3 as rapidly as it was formed, leaving no SO_3 to appear in the gas phase.

Figure 3 shows the effect of gas velocity over the surface. Decreasing the velocity by 10 times, from 12 feet per second to 1.2 feet per second, increased the SO_3 concentration at 0.005 inch from the surface from less than 200 ppm to more than 1600 ppm. It is evident that velocity has a strong effect on the SO_3 level, almost certainly because the residence time is greater near the surface at low gas velocity, and more time is available to approach equilibrium. It is evident, too, that the same effect should take place beneath a deposit, where low gas velocities likewise should lead to high levels of SO_3 .

No data are available on the SO_3 level to be expected directly on the surface rather than 0.005 inch away in the gas stream. The steep gradient near the surface suggests that the SO_3 might reach equilibrium concentrations where the gas mixture actually contacts the catalytically active surface.

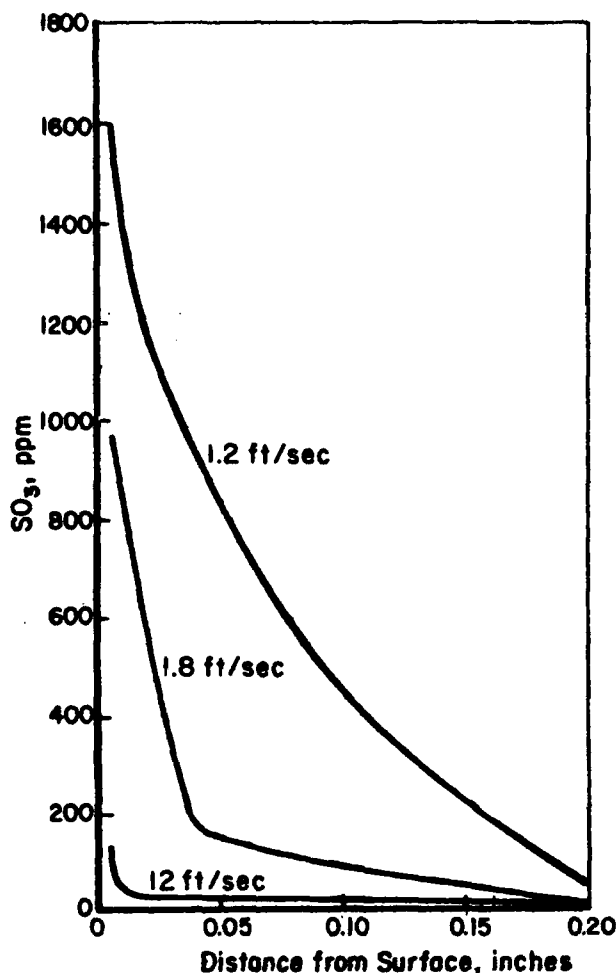


FIGURE 3. EFFECT OF FLOW VELOCITY ON SO_3 GRADIENT ABOVE Fe_2O_3

Catalytic Activity of Fly Ash

Fly ash is often considered catalytically active in converting SO_2 to SO_3 . This property has been blamed for some cases of corrosion where trisulfates have been formed within an ash deposit. Tests of this characteristic were made here by measuring the SO_3 downstream of coated surfaces exposed to flue gas from the burning of sulfur-doped No. 2 fuel oil. The control was an iron surface coated with Fe_2O_3 .

Table 2 illustrates the relative capabilities of three fly ashes compared with Fe_2O_3 in increasing the SO_3 in flue gas passing over these materials, under similar laboratory conditions of temperature, flue gas composition, gas velocity, and sampling point downstream of the deposit. It is apparent that much less SO_3 is present over fly ash than over Fe_2O_3 , and that the iron content of the fly ash expressed as equivalent Fe_2O_3 is not a good measure of the catalytic properties of the fly ash as far as SO_3 put into the gas stream is concerned. Indeed, Joppa fly ash with the highest equivalent Fe_2O_3 content was markedly less "catalytic" than either of the two other fly ashes containing half as much equivalent Fe_2O_3 .

TABLE 2. COMPARATIVE CATALYTIC ACTIVITY OF FLY ASHES AND IRON OXIDE

Material	Equivalent Fe_2O_3 , percent (a)	Total Alkalies, percent	pH of Deposit (b)	Increase in SO_3 at 1200 F, ppm	Percentage of Level with Fe_2O_3
Fe_2O_3	100	0	-	45	100
Port Jefferson Fly Ash	17.0	2.9	4.5	13	29
Astoria Fly Ash	16.8	2.7	4.2	8	18
Joppa Fly Ash	30.4	2.4	3.0	2	4

(a) Total iron content calculated as Fe_2O_3

(b) After 5 hours at 1200 F in simulated flue gas.

Because these fly ashes contain some alkalis, it is reasonable to expect that a part of any SO_3 produced by catalysis may have reacted within the deposit to form complex sulfates, in which case the SO_3 downstream would not have increased as much as if no alkalis were present. The lower alkali content of the Joppa fly ash suggests that this action should have been less than in the other fly ashes, but the lower pH of the Joppa deposit shows that more SO_3 was actually captured. The amount of trisulfates formed within the fly ashes was not determined, but if appreciable quantities had been present, the pH would have been as low as 1.0.

Also, because a half to a fourth of the iron content of fly ash is FeO , with the remainder present as Fe_2O_3 , it is evident that the total equivalent Fe_2O_3 in fly ash is not a measure of its ability to catalyze gas reactions. The way in which iron is present in fly ash, and the surface conditions, particle size, and the other constituents in the ash, particularly alkalis, all will affect the apparent catalytic behavior of fly ash as shown by SO_3 added to the flue gas. Hence, although fly ashes can help oxidize SO_2 to SO_3 , such action is not predictable in increasing the SO_3 content of flue gas downstream of an ash deposit.

Catalysis and Reactivity of Surfaces

As was pointed out earlier, mixtures of Na_2SO_4 and of NaOH with Fe_2O_3 did not lead to increased amounts of SO_3 in the gas stream when gas mixtures containing SO_2 and O_2 flowed over such surfaces, although Fe_2O_3 by itself was extremely active. The conclusion reached was that the mixture was capturing SO_3 as rapidly as it was produced, and that these added salts had not destroyed the catalytic activity of the Fe_2O_3 . Along similar lines, a series of tests investigated the relative reactivity and catalytic ability of Fe_3O_4 compared with Fe_2O_3 , and the further effect of other materials added to these oxides.

Based on measurements of SO_3 near a surface by sampling with the microprobe, it was shown that Fe_3O_4 was much less catalytic than Fe_2O_3 . For example, at 1100 F and 0.005 inch from the surface, a layer of Fe_2O_3 on an inert Vycor substrate led to 1600 ppm SO_3 in the gas stream, whereas under the same conditions with Fe_3O_4 , only 80 ppm SO_3 was found. Oxidized iron surfaces produced 1010 ppm SO_3 , showing that the surface was not solely Fe_2O_3 , and that some Fe_3O_4 was present in the exposed surface through interaction with the iron substrate. A mixture of equal parts of Fe_2O_3 and Fe_3O_4 on a Vycor substrate produced 820 ppm SO_3 . It is evident from these data that Fe_2O_3 is much more catalytic than Fe_3O_4 .

As to reactivity, just the opposite occurs. With S^{36}O_2 in a mixture of N_2 , O_2 , and SO_2 passed over surfaces at 1100 F, more than twice as much sulfur was captured by Fe_3O_4 as by Fe_2O_3 , while only half as much radioactive SO_3 was found in the gas stream over Fe_3O_4 as over Fe_2O_3 . When alkalis were present, the difference was even greater, but reliable quantitative data are too few to draw firm conclusions. It appears evident, however, that the state of oxidation of the iron on the surface of ferritic alloys has a large effect on the reactivity of the scale with deposited alkalis and the sulfur oxides in flue gas. As a general conclusion, considering that Fe_3O_4 is formed before Fe_2O_3 when an iron surface is oxidized, the Fe_3O_4 may react with alkalis to produce compounds leading to the trisulfates as the initial step in corrosion before any appreciable quantity of Fe_2O_3 is present.

This action may be related in some way to the so-called "induction period" in boiler furnaces, where a superheater may foul less rapidly during its first six months of operation than when it has been in service for several years. Since there is a gradual transition from Fe_3O_4 to Fe_2O_3 in the exposed part of the oxide film on a superheater element, and since Fe_3O_4 and Fe_2O_3 behave so differently, it is reasonable to postulate that this change may be responsible for the induction period. This point has not been investigated, but it would be worth consideration in any future studies along these lines.

Relative Reactivity of SO_3 and SO_2

Earlier opinions that SO_3 was more responsible for corrosion than SO_2 , even though there is 100 times more SO_2 than SO_3 in flue gas, have been supported by quantitative measurements of the reactivity of these sulfur oxides using S^{35}O_3 or S^{35}O_2 as a tracer. In many series of tests, covering a wide range of conditions, it has been shown that SO_3 is so much more reactive than SO_2 that for all practical purposes the SO_2 is insignificant when even traces of SO_3 are present.

In a typical experiment, measurements were made of the radioactive count of surfaces exposed to a simulated flue gas mixture of 30 ppm SO_3 containing a very small amount of S^{35}O_3 , 2500 ppm SO_2 , 3 percent O_2 , and the remainder N_2 . Under the same test conditions, the radioactive count was measured of surfaces exposed to 2500 ppm SO_2 containing S^{35}O_2 , but with no SO_3 present. By comparing these radioactive count rates, a measure is obtained of the relative reactivity of SO_3 and SO_2 , expressed as a "reactivity ratio".

When these gas mixtures were passed over a surface made up of a mixture of Fe_2O_3 and Na_2SO_4 , the reactivity ratio at 1100 F was 970; at 1200 F it was 2400. Hence, despite the fact that there was 83 times as much SO_2 as SO_3 in the initial gas stream, the SO_3 captured by the surface was 970 times more than with SO_2 at 1100 F, and 2400 times more at 1200 F.

The influence of temperature is marked, the maximum pickup with SO_3 taking place at 1200 F, and the minimum with SO_2 at 1150 F. Increasing the amount of SO_2 in the flue gas naturally increases the amount of SO_2 picked up by the surface, but even when 5.3 percent SO_2 was present in one set of experiments, 30 ppm SO_3 still was 50 times more reactive than the SO_2 .

Variations in the composition of the surface also affect the reactivity ratio. With a gas mixture containing 5.8 percent SO_2 and 19.4 percent O_2 at 1100 F, as was used with some tests, mixtures of K_2SO_4 and Fe_2O_3 showed the 30 ppm to SO_3 to be 22 times more reactive than the SO_2 , whereas the reactivity ratio was 17 for Na_2SO_4 and Fe_2O_3 . Hence, with potassium present, there is an even greater difference between SO_3 and SO_2 in reactivity. This also supports other work showing potassium to be more active than sodium in causing corrosion.

The main conclusion here is that even traces of SO_3 in flue gas can lead to reaction with the surface, whereas SO_2 is much less likely to react. It is evident, however, that when SO_3 is absent, SO_2 cannot be ignored.

SO₃ Concentration Beneath Deposits

Although many roles are assigned to deposits in leading to metal wastage, the exact mechanism by which deposits establish conditions causing corrosion are not known. It is thought generally that several mechanisms are involved, any one of which may favor corrosion of the underlying metal. For example, the trisulfates can form within deposits by reaction between alkalies and the Fe₂O₃ originally in the fly ash, but the trisulfates also can form on metal surfaces at the expense of the Fe₂O₃ layer on the metal. Deposits also may serve to increase the alkali concentration on the cooler metal surface because of migration of sodium and potassium through the temperature gradient found in all deposits. And, as mentioned earlier, deposits may establish a nearly stagnant environment at the surface of the metal. This would provide ample time for high SO₃ concentrations to be developed as the result of SO₂ and O₂ diffusing through the deposit or migrating through cracks and imperfections in the ash layer.

Measurements of SO₃ beneath simulated deposits have been made in this study to get some measure of how important this latter factor might be. In these experiments a mixture of materials simulating a deposit was packed around an iron-covered sampling tube at the center of a stainless-steel box-like container. All the flue gas drawn through the sampler passed through the deposit and over the iron surface before being analyzed. The assembly was heated in the fuel-fired furnace burning sulfur-doped No. 2 fuel oil, so that the flue gas was similar to that in large furnaces. Temperature was measured with a thermocouple peened to the iron tube beneath the deposit. In all, 23 such tests were made, with simulated deposits varying from Fe₂O₃ alone to two-layer deposits containing five constituents. Besides measuring SO₃ beneath the deposit, each specimen was examined microscopically for the presence of trisulfates after the 5-hour tests.

The broad conclusions drawn from these tests are:

- A deposit of Fe₂O₃ alone increased the SO₃ concentration beneath the deposit by three to five times. No trisulfates were formed because no alkalies were present.
- In a two-layer deposit with Fe₂O₃ above a mixture of Na₂SO₄ and K₂SO₄, the SO₃ level beneath the deposit was four times greater than in the flue gas, with barely detectable amounts of trisulfates formed in 5 hours.
- Whenever mixtures of alkali sulfates and Fe₂O₃ were present and there was no perceptible increase in SO₃ beneath the deposit, from 2 percent to 5 percent trisulfates generally were formed during a 5-hour test.
- When similar mixtures led to the formation of a distinct white layer at test temperatures between 1000 F and 1025 F, for reasons not yet clear, one-third of the layer in one test and half the layer in another were trisulfates, even though the test duration was only 5 hours.

Addition of calcium or magnesium carbonates or sulfates, or of kaolin, appear to have little effect on SO₃ formation, once the carbonates are converted to sulfates. Despite the presence of these diluents, trisulfates generally were produced in such mixtures when no increase in SO₃ levels was observed beneath the deposits.

- The same general effects occur in two-layer systems as with single-layer mixtures, distribution of components in the layers apparently having little effect on the behavior of the deposit.
- Vanadium as V_2O_5 mixed with Al_2O_3 increased the SO_3 by about one half. With V_2O_5 mixed with Na_2CO_3 , the SO_3 level was tripled, and the deposit was molten at 1015 F, presumably through the formation of sodium vanadyl vanadate. In three tests where V_2O_5 was present and alkalies were also available, strongly fused deposits resulted at temperatures below 1100 F.
- Temperature plays an important part, with the larger quantities of trisulfate usually being formed below 1050 F. At higher temperatures, the tendency is to increase the SO_3 concentration.

Variations were large in these tests, and usually it was not possible to get close agreement between duplicate runs. Nevertheless, the trends noted here generally are consistent.

Trisulfates in Deposits From Operating Boiler Furnaces and Gas Turbines

Through the cooperation of the Research Committee on Corrosion and Deposits from Combustion Gases, a number of samples of deposits from operating units were made available for examination. In addition, special samples were collected at Joppa in September, 1967 during a routine outage. These Joppa samples were examined critically; each of the others was checked for the presence of trisulfates using the highly sensitive index-of-refraction technique.

Most detailed examination was made of a specimen from Joppa taken from a ferritic reheater tube where the metal temperature was assumed to be 1025 F, and where the deposit had a distinct white layer about 1/32-inch from the tube metal. Photomicrographs and examination with an electron microprobe analyzer showed that the white layer was not homogeneous, but was made up of a large number of tiny discrete particles of widely varying composition. The electron probe scans showed that spots rich in potassium also were rich in sulfur, with moderately high sodium and iron contents, suggesting that complex alkali-iron-sulfur compounds were present in microscopically small areas. Overall evaluation of the white layer showed it to contain up to 5 percent potassium in some areas; up to 2 percent sodium; large amounts of sulfur, as much as 35 percent in some spots; and small amounts of iron in an unidentified form. Silica and alumina were high as would be expected because the deposit is mainly fly ash. The thin layer between this white layer and the reheater tube contained about 35 percent sulfur and 50 percent iron, reflecting the presence of FeS .

Microscopic examination of the Joppa specimen showed a large amount of well-formed trisulfate crystals in the white layer, identified by their index of refraction. Based on the electron-probe studies and the microscope examination, it was concluded that the trisulfates were formed both from the iron oxide in the fly ash and from that occurring through normal oxidation of the ferritic reheater tube.

Samples of deposits from other stations also were examined in the laboratory. They occasionally showed trisulfates in small crystallites, but there seemed to be a preponderance of anisotropic material nearly matching the trisulfates in index of refraction. This material, or substances like it, has also been found in laboratory tests, where it has been considered an "intermediate" in the formation of trisulfates. It is possible that this intermediate may be $\text{NaFe}(\text{SO}_4)_2$.

Samples from gas turbines showed no trisulfates, with Fe_2O_3 as a major constituent. No attempts were made to identify the many vanadium compounds evidently present.

Samples from two oil-fired boilers showed no trisulfate in the deposit. In one case, MgO had been added and the deposit was found to contain Na_2SO_4 . In the other, the gas temperature had been 1400 F, too high to permit trisulfate formation.

No obvious conclusions can be drawn from these examinations, other than that research tools are now available whereby deposits can be examined more critically than in the past. In particular, the ability to detect trace amounts of the alkali iron trisulfates in deposits or on tube surfaces should be highly useful to boiler furnace operators. Using the index-of-refraction technique on samples taken on a consistent basis should permit operators to relate corrosion tendency to the operating conditions in their units.

THE FUTURE

These six years spent investigating metal wastage have established with fair assurance the most important factors in the corrosion of metals in hot flue-gas atmospheres. It has been shown, for instance, that low excess air is the only practical way of modifying the combustion process to eliminate external corrosion. Useful presently only when burning fuel oil, low excess air should be equally effective with pulverized coal if the engineering problems of mixing fuel and air, and of providing sufficient time, temperature, and turbulence could be solved.

It has been confirmed, too, that conditions presently leading to serious corrosion are connected with the development of a liquid phase on the metal surface - generally complex sulfates in the case of coal firing, and, when oil is burned, the formation of molten vanadates as well. Short of removing alkalis, sulfur, and vanadium from fuels, or of adding such materials as MgO in oil-fired units, no way has been found of preventing the accumulation of these substances beneath deposits. It does not appear likely now that it will ever be economically feasible for large-scale power generation to provide clean fuels from which these elements have been removed.

Temperatures presently established for steam generation are almost precisely in the range where external corrosion can be most severe. Increasing steam temperature markedly, say to more than 1300 F, should eliminate corrosion in superheaters by complex sulfates, but would increase hazards with vanadium. Also, there would have to be a transition section somewhere within the boiler where metal surfaces would be in the critical temperature range. Operating at lower temperatures than the present 1000 F should be effective in eliminating vanadium-type corrosion, but metal loss caused by the alkali iron trisulfates and the alkali pyrosulfates may continue to be troublesome at temperatures even below 1000 F. Hence unless a radical step can be made in raising steam temperatures, with all its attendant costs for higher-duty alloys, corrosion can continue to be troublesome.

With the demonstration here that low gas velocities over a surface are necessary to form SO_3 at concentrations great enough to produce trisulfates, one explanation exists on the way in which deposits lead to corrosion - they provide the stagnant conditions on the tube surface whereby high SO_3 levels are reached. Where no deposits are present, the SO_2 in flue gas flowing over surfaces at velocities as high as 100 feet per second cannot oxidize appreciably to SO_3 . Hence if ash could be kept from depositing on surfaces, or if the deposits were fractured so badly or were so weakly attached that flue gas could flow at high velocity over the metal surface, corrosion would be unlikely. Similarly, if some method could be devised to pass air beneath deposits to sweep out the flue gas, then SO_3 formation might be eliminated, and hence corrosion. Engineering-wise, it will be difficult to devise methods of ventilating metal surfaces beneath deposits.

Another approach would be to eliminate deposits entirely. This would pose difficult problems too, yet no real effort seems to have been made, except quite theoretically, to investigate how and why ash particles in a gas stream approach a surface and attach themselves to it. Aerodynamic conditions have been analyzed and mechanisms of deposition have been postulated. But physical analysis is not so far advanced. What appears needed now is research on the physical processes involved in moving particles from a gas stream to a cooler solid surface, the means by which solids accumulate on such surfaces, and the likelihood of interrupting these processes by some workable method.

The next step in minimizing corrosion should be a practical study of ash-deposition processes, of means of interfering with deposition, and of devising methods of keeping metal surfaces clean by some more direct method than blowing with jets of steam. As an alternative study, consideration should be given to schemes for admitting air beneath deposits. Both will require great ingenuity and genuine inventiveness, but a practical solution of either could well solve the metal wastage problem in boiler furnaces. In gas turbines, cooling air for controlling blade temperature, if distributed uniformly over the metal surface, also may be helpful in decreasing deposition, but corrosion might not be decreased because SO_3 here is not so troublesome as at lower temperatures.

As a worthwhile project, then, the Committee should consider work on physical deposition processes, with the intent to eliminate corrosion by eliminating deposits that provide a corrosion environment. Such a study if successful could reap great dividends, not only in corrosion prevention, but in controlled heat transfer as well.

REPORTS AND PUBLICATIONS

In addition to monthly letter reports that have gone regularly to the Committee to keep them abreast of day-to-day developments in the laboratory, three Summary Reports have been issued at six-month intervals. These have been divided into two sections, on General Review and on Technical Details, to increase their usefulness to different kinds of readers.

Publication in the technical press of the results of this research has been encouraged by the Committee. Accordingly, four technical papers by Battelle staff members have been published in the Journal of Engineering for Power of the ASME, and one paper has been published by the American Petroleum Institute. A paper was also presented at the 1967 Annual Meeting of the American Institute of Chemical Engineers. George C. Wiedersum, as Chairman of the Committee, reviewed the Battelle work in a paper at the 1967 Joint Power Generation Conference. In addition to these, a special report was distributed to the Committee in 1967 describing in detail the special analytical procedures used at Battelle in analyzing small volumes of gas for SO_2 and SO_3 . Presently a manuscript is being prepared for sponsorship by the Committee at the 1968 Winter Annual Meeting of ASME.

Following is a listing of these papers:

"Basic Problems in the Formation of Sulfates in Boiler Furnaces", by William T. Reid. Trans. ASME, J. Eng. Power, vol. 89, Series A, no. 2, April, 1967, pp. 283-287.

"High-Temperature Corrosion Studies in an Oil-Fired Laboratory Combustor", by Richard E. Barrett. Trans. ASME, J. Eng. Power, vol. 89, Series A, no. 2, April, 1967, pp. 288-296.

"Interactions in Sulphur Oxide-Iron Oxide Systems", by A. Levy and E. L. Merryman. Trans. ASME, J. Eng. Power, vol. 89, Series A, no. 2, April, 1967, pp. 297-303.

"Sulfur Oxide Reactions: Radioactive Sulfur and Microprobe Studies of Corrosion and Deposits", by H. H. Krause, A. Levy, and William T. Reid. Trans. ASME, J. Eng. Power, vol. 90, Series A, no. 1, January, 1968, pp. 38-44.

"Present Status of Knowledge of High-Temperature Corrosion from Vanadium and Sulfur in Combustion Gases", by William T. Reid, P. D. Miller, and H. H. Krause. Proc. Div. Refining, vol. 47, 1967, American Petroleum Institute, pp. 404-419.

"Mechanisms of Formation of Sulfur Oxides in Combustion", by A. Levy, E. L. Merryman, and William T. Reid. Presented at 60th Annual Meeting of AIChE, November 26-30, 1967.

"Corrosion and Deposits from Combustion Gases - A Review", by George C. Wiedersum. Presented at Joint Power Generation Conference, September 24-28, 1967.

"A Microprocedure for the Analysis of SO_2 and SO_3 ", by E. L. Merryman, A. Levy, and William T. Reid. Distributed to the Committee, April 24, 1967.

"Radioactive Sulfur Oxide Studies of External Corrosion Reactions on Surfaces", by H. H. Krause, A. Levy, and William T. Reid. To be presented at the 1968 ASME Winter Annual Meeting, December 1-5, 1968.

The Appendix to this report lists all of the publications from this work since 1962 when the project began.

SURFACE INVESTIGATIONS

by

H. H. Krause

SULFUR-35 STUDIES

A major part of the investigation here of reactions on surfaces has considered the relative reactivity of SO_3 and SO_2 . Because there is so much less SO_3 than SO_2 in flue gas, it has been important to learn whether the SO_3 indeed is the main cause of corrosion, or if SO_2 also may be involved, and to what extent. Some control may be exerted over the excessive occurrence of SO_3 in flue gas, but the SO_2 content cannot be reduced significantly except by selecting fuels containing less sulfur, or, more recently, by adding massive doses of limestone or dolomite to the hot flue gas. Hence, over the past six months, a continuing effort has been carried out on the relative reactivity of SO_3 and SO_2 with surfaces. The experimental apparatus and procedures used in this work with S^{35} were the same as described in the three preceding Summary Reports.

The effect has been studied of lower concentrations of SO_2 and oxygen than were used in the earlier experiments. The effect of temperatures down to 900 F was examined to include reactions involving magnetic (gamma) Fe_2O_3 , an intermediate stage in the oxidation of iron. In addition, mixtures with Na_2SO_4 initially containing Fe_3O_4 were investigated.

Effect of Temperature

The study of the effect of temperature on the reactivity of SO_3 and SO_2 with a mixture of Na_2SO_4 - Fe_2O_3 (3 to 1 mol ratio) was extended down to 900 F. The gas mixture used was the same as in earlier experiments: 74.8 percent N_2 , 19.4 percent O_2 , 5.8 percent SO_2 , and when SO_3 was used, 30 ppm.

The reactivity of the $\text{SO}_2 + \text{O}_2$ with the surface at 900 F was the greatest that has been observed over the temperature range studied (900 F to 1300 F). However, although trisulfate formation has been noted on wall tubes where metal temperature is less than 800 F, generally the rate of formation is low for the trisulfates below 900 F. Hence, when the products of the reaction were examined by X-ray diffraction and by optical microscopy, it was found that some sodium pyrosulfate, $\text{Na}_2\text{S}_2\text{O}_7$, had been formed but no trisulfates were found. The pyrosulfate has a limited range of stability, and would not be formed at higher temperatures, where the trisulfate is stable. When the results at 900 F are compared with those at higher temperatures, as shown by Figure 1 of the Third Summary Report, the 900 F point falls on the curve established by the data at the higher temperatures.

Although SO_2 reactivity was high at 900 F, when 30 ppm SO_3 was added to the gas stream, the reactivity as indicated by the radioactive count was 11.8 times greater. The SO_3 reactivity at 900 F was greater than that at 1000 F, 1100 F, and 1300 F, but only 60 percent of that observed at 1200 F.

The radioactive counts and the "reactivity ratios" for SO_3 and SO_2 at temperatures from 900 F to 1300 F are shown in Table 3. The data from 1000 F to 1300 F have been reported previously, and are included again to show the radioactive counts obtained over the entire temperature range, and to compare the reactivity ratios. This ratio is based on the radioactive counts observed in the surface exposed to the gas stream, and is determined as follows:

Reactivity Ratio =

$$\frac{\text{Radioactive Count of Surface Exposed to } \text{S}^{35}\text{O}_3 \text{ with } \text{SO}_2 \text{ and } \text{O}_2 \text{ Present}}{\text{Radioactive Count of Surface Exposed to } \text{S}^{35}\text{O}_2 \text{ with } \text{O}_2 \text{ Present}}$$

TABLE 3. REACTIVITY OF SO_3 (30 ppm) AND SO_2 (5.8%) TOWARD $\text{Na}_2\text{SO}_4\text{-Fe}_2\text{O}_3$ MIXTURE AT DIFFERENT TEMPERATURES

Temperature, F	Radioactive Count, thousands/min		Reactivity Ratio
	S^{35}O_2	$\text{S}^{35}\text{O}_3 + \text{SO}_2$	
900	184	2170	11.8
1000	117	1475	12.6
1100	69.3	1160	16.8
1200	72.1	3620	50.2
1250	80.6	1180	14.6
1300	115	1550	13.5

In all of these tests, SO_3 has been used at a concentration of 30 ppm, and the SO_2 and O_2 concentrations have been changed in different runs. Thus the "reactivity ratio" measures the increase in reactivity when 30 ppm SO_3 are added to the gas mixture. Although the S^{35}O_3 and S^{35}O_2 make up only a small part of the SO_3 and SO_2 in the respective gas streams, the non-radioactive sulfur oxides react in the same way as the S^{35} oxides, so these ratios express the relative reactivities of the whole system. While there are small increases in the reactivity ratios from 900 F to 1100 F, the large increase at 1200 F expresses the preponderant SO_3 reactivity at this temperature. The drop in reactivity above 1200 F in this system is related to the decomposition of the trisulfate at higher temperatures. The SO_2 reactivity goes through a minimum in about the same temperature range that the SO_3 reactivity is a maximum, showing that the corrosion that has been found to occur can be attributed primarily to SO_3 .

Effect of SO₂ and O₂ Concentration

Experiments carried out earlier in the program were done with 5.8 percent SO₂ in the gas mixture and with oxygen at 19-20 percent, as in air. These concentrations were used because they allowed comparison with the earlier flame studies. Both these SO₂ and oxygen concentrations are higher than in flue gases, so additional experiments were made at lower levels, some with the SO₂ reduced to 2500 ppm, and some with oxygen decreased to 3 percent, corresponding to boiler operation with 15 percent excess air. When SO₃ was used, 30 ppm were added. These runs were made at 1100 F and 1200 F only. The surfaces consisted of the same mixture of Na₂SO₄ and Fe₂O₃ in a 3 to 1 mol ratio, which is the stoichiometry for trisulfate formation, that has been used throughout these experiments.

The results are shown in Table 4, in terms of the reactivity ratios as defined above. When the SO₂ was reduced to 2500 ppm and the oxygen was kept high, addition of SO₃ increased the reactivity greatly, both at 1100 F and at 1200 F.

TABLE 4. EFFECT OF SO₂ AND O₂ CONCENTRATION
ON REACTIVITY OF SO₂ AND SO₃ (a)

SO ₂ , v/o	O ₂ , v/o	SO ₃ /SO ₂ "Reactivity Ratio"	
		1100 F	1200 F
5.8	19.4	16.8	50.2
0.25	20.8	360	1040
0.25	3.0	970	2400

(a) SO₃ concentration was 30 ppm.

In fact, the reactivity ratios observed at 2500 ppm SO₂ were approximately what would be expected by a linear extrapolation of the data obtained earlier at 5.8 percent SO₂. In addition, the reactivity with the surface increased rapidly from 1100 F to 1200 F when the SO₃ was added. The increase in reactivity with temperature was slightly greater at the lower SO₂ concentration, as shown by the reactivity of the SO₃ + SO₂ mixture being 3.57 times greater at 1200 F than at 1100 F with 2500 ppm SO₂, and only 3.12 times greater with 5.8 percent SO₂. The SO₂ reactivity itself was increased slightly in going from 1100 F to 1200 F, just as it was at the higher concentration, amounting to an increase of 1.24 times with 2500 ppm SO₂, and 1.04 times with 5.8 percent SO₂. Thus it is evident that the reactivity at low concentrations of SO₂ with SO₃ present goes through a maximum at 1200 F, just as it did with more SO₂ present. The SO₂ reactivity also goes through a minimum between 1100 F and 1200 F.

When the oxygen available was reduced to 3 percent, the reactivity of SO₂ with the surface was about 1/3 as great at 1100 F and 0.4 as great at 1200 F. This drop must be due to a lowered mass action effect of the excess oxygen. When 30 ppm SO₃ was present in the gas stream, the reactivity with the surface was,

within experimental error, the same as it had been at the higher level of oxygen. The lower SO_2 reactivity with essentially unchanged SO_3 reactivity is reflected in the higher reactivity ratios shown in Table 4 for these conditions.

Some runs also were made at the 3 percent oxygen concentration with 30 ppm SO_3 but no SO_2 present. These results were compared with those found when the gas stream also contained 2500 ppm SO_2 . There was a slight increase in reactivity at 1100 F when no SO_2 was present. At 1200 F, the contribution of the SO_2 was even less, and leaving it out of the gas mixture gave essentially the same results as when it was present.

This series of experiments has served to emphasize the fact that the 30 ppm of SO_3 formed in the flame is a more serious factor in the formation of corrosive deposits by hundreds of times than are the much larger amounts of SO_2 normally in flue gas even in the presence of excess oxygen.

Reactivity of Magnetic (γ) Fe_2O_3

In an effort to study the role of intermediates leading to trisulfate formation, experiments were carried out in which gamma- Fe_2O_3 was substituted for the common alpha- Fe_2O_3 in the mixture with Na_2SO_4 . Gamma- Fe_2O_3 is the magnetic form of Fe_2O_3 and has the same structure as Fe_3O_4 , the common black magnetic oxide. In the oxidation of iron, the brown gamma- Fe_2O_3 lies between Fe_3O_4 and alpha- Fe_2O_3 , the ordinary red oxide:

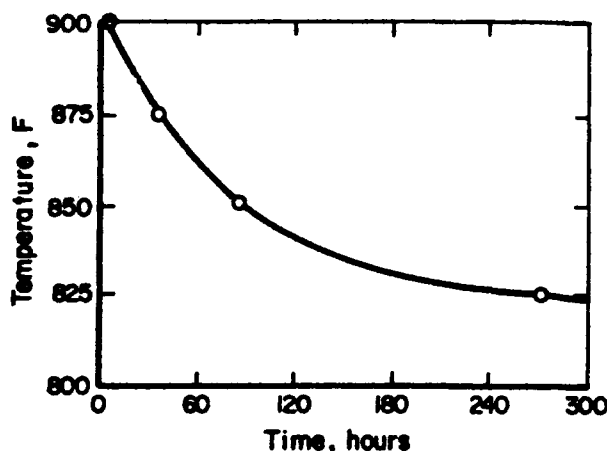


FIGURE 4. RATE OF CONVERSION OF GAMMA- Fe_2O_3 TO ALPHA- Fe_2O_3 AS A FUNCTION OF TEMPERATURE

Gamma- Fe_2O_3 results from relatively low-temperature oxidation of Fe_3O_4 (below 750 F), thereby retaining the crystal structure of the latter compound. When heated, gamma- Fe_2O_3 changes into alpha- Fe_2O_3 . This transition occurs in less than an hour at 1000 F and after about 4 hours at 900 F. At temperatures below 900 F, the change takes place very slowly, as shown in Figure 4. There is a good chance that a boiler surface which does not get heated beyond 800 F can have gamma- Fe_2O_3 as a reactive component.

To preserve the magnetic oxide structure during the entire experiment made here, the tests were made at 900 F and compared with similar tests using ordinary Fe_2O_3 . The gas mixture used was 74.8 percent N_2 , 19.4 percent O_2 , and 5.8 percent SO_2 , with 30 ppm SO_3 added in some tests.

The results showed that the gamma- $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4$ mixture (1 to 3 mol ratio) was more reactive both with SO_2 and SO_3 than was the alpha- $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4$ mixture. The data are compared graphically in Figure 5. The SO_2 reactivity with

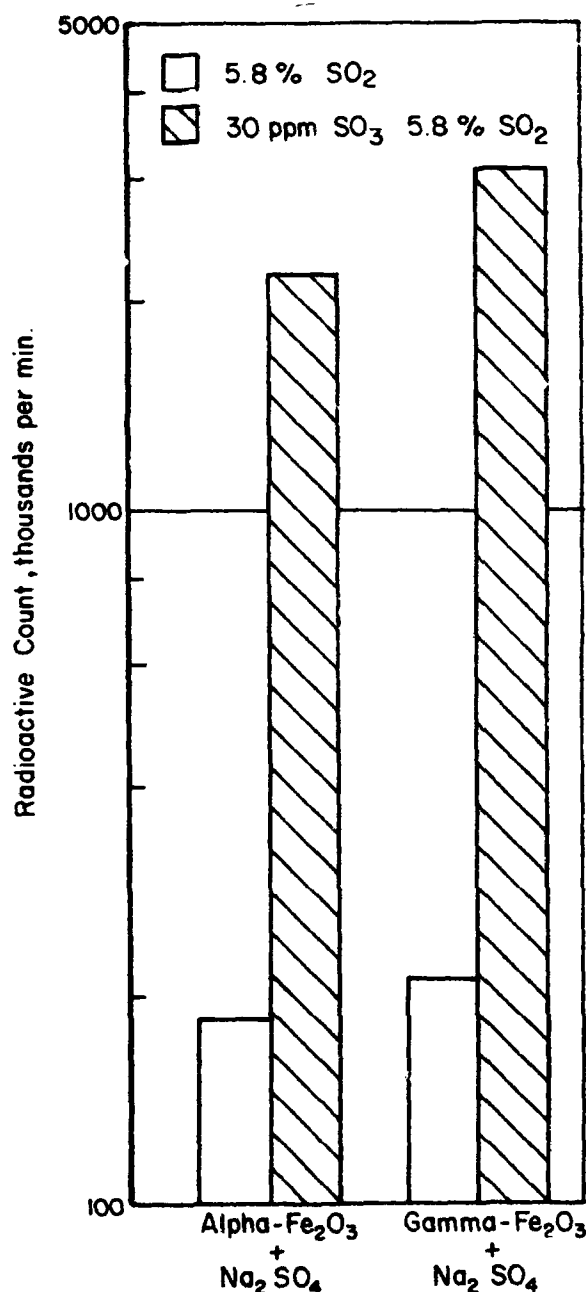


FIGURE 5. EFFECT OF TYPE OF Fe_2O_3 ON REACTIVITY OF SO_2 AND SO_3 WITH Na_2SO_4 - Fe_2O_3 SURFACE AT 900 F

the surface was 1.2 times as great for the gamma Fe_2O_3 mixture as for the alpha- Fe_2O_3 mixture, and when 30 ppm SO_3 were added, the reactivity with the gamma type became 1.4 times greater. The reactivity ratios as defined earlier were 14.2 for the gamma- Fe_2O_3 as compared with 11.8 for the alpha- Fe_2O_3 . Because these reactions occurred at 900 F, trisulfates would not be expected as products. Examination of the reaction products by X-ray diffraction and optical microscopy showed that sodium pyrosulfate was formed under these conditions.

Figure 6 summarizes the reactions that occur between the alkalis and the different iron oxides in flue gas containing sulfur oxides.

It is based on the fact that SO_3 is mainly responsible for reactions leading to the trisulfates and pyrosulfates. As Fletcher and Gibson(1) had shown earlier, the catalyzed $\text{SO}_2 + \text{O}_2$ reaction was shown to predominate in converting NaCl to Na_2SO_4 ; the same case may occur in converting Na_2O to Na_2SO_4 , as shown at the left of the figure.

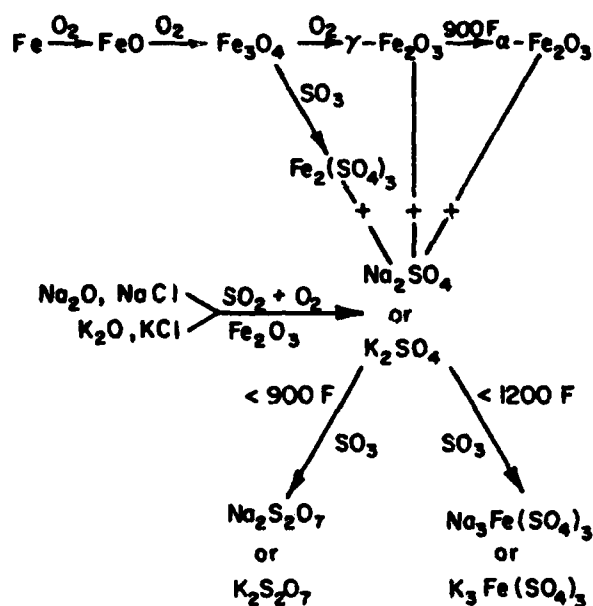


FIGURE 6. REACTION SEQUENCES OF IRON OXIDES AND ALKALIES WITH SULFUR OXIDES

Reactivity of Fe_3O_4

To investigate further the role of intermediates leading to the formation of the trisulfates, experiments were made with a mixture of Fe_3O_4 and Na_2SO_4 (1 to 4.5 mol ratio) at 1100 F. The gas stream consisted of 2500 ppm SO_2 , 20.8 percent O_2 , and 78.9 percent N_2 . When SO_3 was used, 30 ppm were added. Because of the oxidizing conditions, some of the Fe_3O_4 unavoidably was oxidized to Fe_2O_3 during the experiments, so the data are not completely representative of Fe_3O_4 .

The reactivity observed with Fe_3O_4 initially present in the mixture was slightly less than that found when only Fe_2O_3 was present, both with respect to SO_2 and SO_3 . The results are shown in Figure 7. The SO_3/SO_2 "reactivity ratio" for the mixture with Fe_3O_4 is 460, as compared to 360 for the Fe_2O_3 mixture. Earlier in the program it was demonstrated that an Fe_3O_4 surface without Na_2SO_4 is slightly more reactive with sulfur oxides than is a similar Fe_2O_3 surface. The somewhat lower reactivity of the Fe_3O_4 when mixed with Na_2SO_4 can be attributed to the fact that in this case trisulfate is the product, and requires trivalent iron for its formation. Part of the iron in Fe_3O_4 is divalent, and until it is oxidized, the reaction will not be complete. Given sufficient time, the alkali iron trisulfate will be formed, just as it is with Fe_2O_3 present initially.

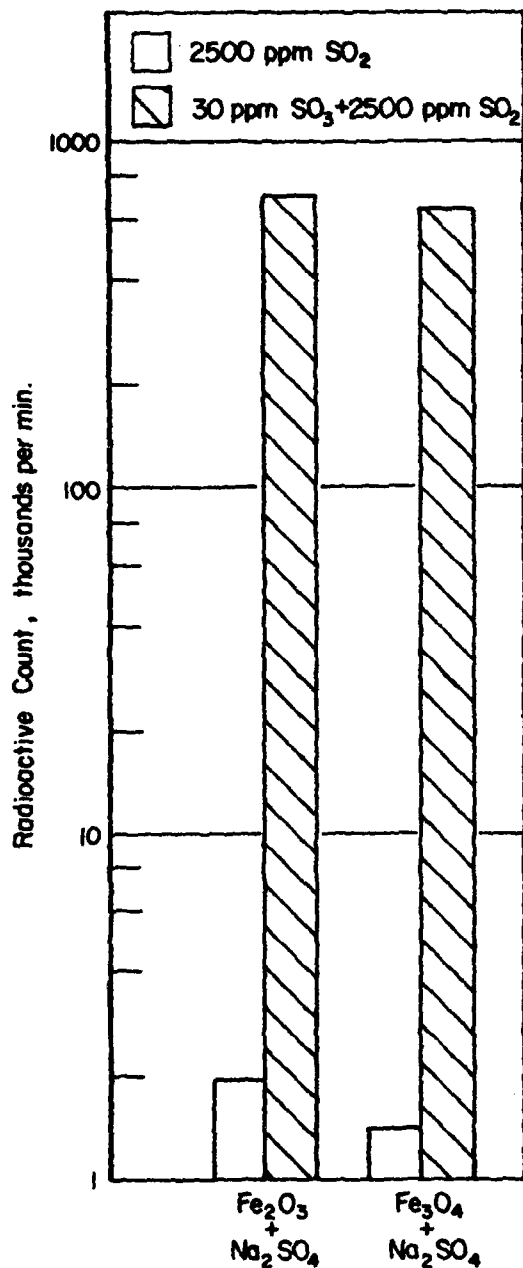


FIGURE 7. REACTIVITY OF SO₂ AND SO₃ WITH SURFACES CONTAINING IRON OXIDES AND Na₂SO₄ AT 1100 F

The general conclusions that can be drawn from all the S³⁵ studies are:

- (1) SO₃ is much more reactive than SO₂ + O₂ for all the surfaces and under all the conditions studied.
- (2) As a function of temperature, the SO₂ reactivity is a minimum between 1100 F and 1200 F. The SO₃ reactivity reaches a sharp maximum at 1200 F when Fe₂O₃ and Na₂SO₄ are present.
- (3) The reactivity of surfaces at 1100 F to the sulfur oxides in flue gas, in decreasing order, is:
 - a. Fe₂O₃ + K₂SO₄
 - b. Oxidized steel + Na₂SO₄
 - c. Fe₂O₃ + Na₂SO₄
 - d. Fe₃O₄ + Na₂SO₄
 - e. Oxidized steel
 - f. Na₂SO₄
 - g. Fe₃O₄
 - h. Fe₂O₃

IDENTIFICATION OF COMPOUNDS IN BOILER DEPOSITS

Samples of boiler deposits obtained from the Public Service Electric and Gas Company of New Jersey were examined for the presence of alkali iron trisulfates, using the index of refraction technique developed on this program. These deposits came from an oil-fired boiler in which dry dead-burned MgO was injected in an amount to provide a Mg/V ratio of about 2. Both inner and outer deposit layers from two different tube locations were included: (1) reheater, second pendant inlet tube, and (2) high-temperature superheater, second pendant inlet tube. Two other outer deposit layers from the high-temperature superheater also were examined: (1) an outlet screen tube, and (2) first pendant, third tube row. One sample came from a boiler using 80 percent pulverized coal and 20 percent petroleum coke.

No alkali iron trisulfates were detected in any of these deposits, although Na_2SO_4 was identified in the inner deposit layers of both the reheater and high-temperature superheater samples. There was also indication of Na_2SO_4 in the outer deposits of the high-temperature superheater screen tube and the first pendant, third tube row. Because of the number of possible magnesium vanadates and hydrated magnesium sulfates, no effort was made to identify any of these compounds in the deposits.

Boiler deposit specimens obtained from American Oil Company, Whiting, Indiana, also were examined for the presence of alkali iron trisulfates. The deposits were obtained from an oil-fired boiler burning fuel containing about 2.5 percent sulfur and 65 ppm vanadium. The scale samples and a corroded piece of metal were from a damper exposed to 1400 F flue gases. No trisulfates could be detected in the samples, possibly because the surfaces were at too high a temperature for the trisulfates to persist. Three separate phases could be detected in the scale and scrapings from the corroded piece. They appeared to be the same materials in each case, but definitely were not trisulfate.

FURNACE STUDIES

by

R. E. Barrett

A series of tests was made in the fuel-burning furnace to investigate factors affecting the presence of SO_3 beneath deposits and the formation of the trisulfates.

Figure 8 shows the modified system developed earlier that was used here for determining the SO_3 concentration and the formation of trisulfates beneath deposits. It is essentially the same as the earlier one with a different type of 18-gage iron specimen to simulate a superheater element in providing an oxidizable ferritic surface. The container to hold the deposit being examined is constructed of stainless steel to minimize catalysis on its surfaces.

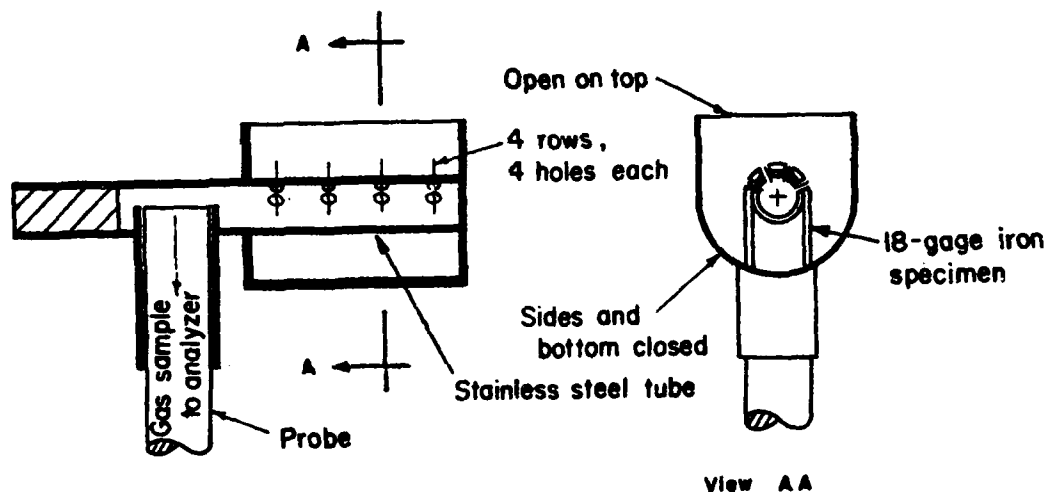


FIGURE 8. SYSTEM FOR DETERMINING EFFECT OF DEPOSITS ON FORMATION OF CORROSIVE CONDITIONS IN FUEL-FIRED FURNACE

The material simulating a deposit is applied over the iron surface to fill this container, providing a layer of deposit about 0.5 inch thick. Only one homogeneous material was present in the holder for most of the tests although a 2-layer deposit was used during several tests. To prevent the furnace flue gas from blowing the material out of the holder, the top layer was dampened initially with acetone.

Each test lasted about five hours after the furnace was preheated and stabilized. Gas-sampling periods were one hour each, to provide enough time to collect 0.1 cubic foot of sample to simulate the limited gas flow expected under a normal deposit. Usually, five such samples were taken during the test with each deposit.

The composition of the deposits varied widely. In tests with Na_2SO_4 , K_2SO_4 , and Fe_2O_3 , the proportions were such as to form the trisulfate. In Tests 7, 8, 9, and 10, where a supposedly inert material was added, such as calcium or magnesium salts or kaolin, the quantity was 9 percent of the total weight of deposit. In Tests 12, 13, and 14, with 2-layer systems, 25 percent of the upper layer was CaSO_4 , MgSO_4 , or kaolin. In the experiments with vanadium, Test 18 contained 25 percent V_2O_5 and 75 percent Al_2O_3 , and Test 20 contained 80 percent V_2O_5 and 20 percent Na_2CO_3 . Tests 16, 17, and 21 each had 8 to 12 percent V_2O_5 present.

Temperatures were measured by a thermocouple imbedded in the iron specimen. Temperature of the upper layer of the deposit was measured in one test and was found to be about 34 F above the measured temperature of the iron specimen. Hence there was an appreciable temperature gradient through the deposit, but a lower one than in boiler furnaces with their greater heat flux.

Results of these tests provide data in three forms:

- (1) SO_3 concentrations measured beneath the deposit,
- (2) physical nature of the deposit material upon removal from the furnace, and
- (3) detection of alkali iron trisulfates in the deposit by optical microscopy techniques.

Figure 9 (pages 28 and 29) shows the SO_3 concentrations in the bulk flue gas stream and as sampled beneath the deposit for the 21 tests run in this series. There is an appreciable variation in SO_3 concentration from test to test with apparently identical deposits at similar temperatures. Variation was also observed from sample to sample during some tests. Such variations can be expected because even minor changes in the way the deposit sinters could affect the SO_3 concentration at the sampling point. Statistically, many more tests would have to be run to account for such random changes. The intent here was to search for broad effects and general trends.

The physical nature of the deposits when removed from the furnace were:

- | | |
|---|-------------------------|
| (a) powdery throughout or some soft chunks | Tests 2,3A,3B,4,5,15,18 |
| (b) chunky or hard layer on top with soft material beneath | Tests 7,8,9,10,11A,21 |
| (c) same as (b), but with a thin white layer between the hard layer and powdery layer | Tests 1,6,19 |

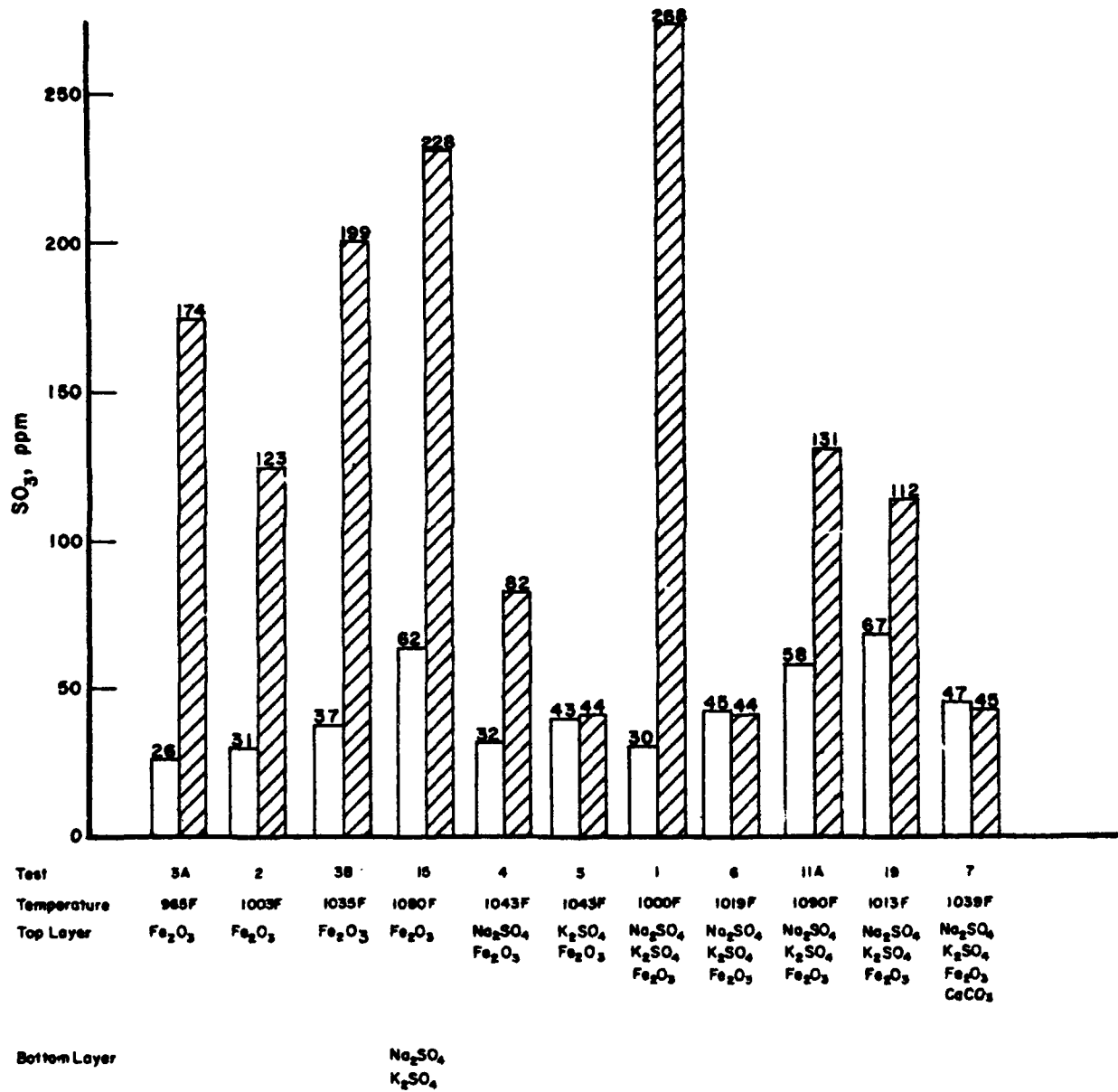
- | | |
|---|----------------|
| (d) hard intermediate layer with a powdery layer above and beneath | Tests 12,13,14 |
| (e) hard throughout, fused | Tests 16,17,20 |
| (f) powdery throughout, but with a few hard chunks around the iron specimen | Test 11B |

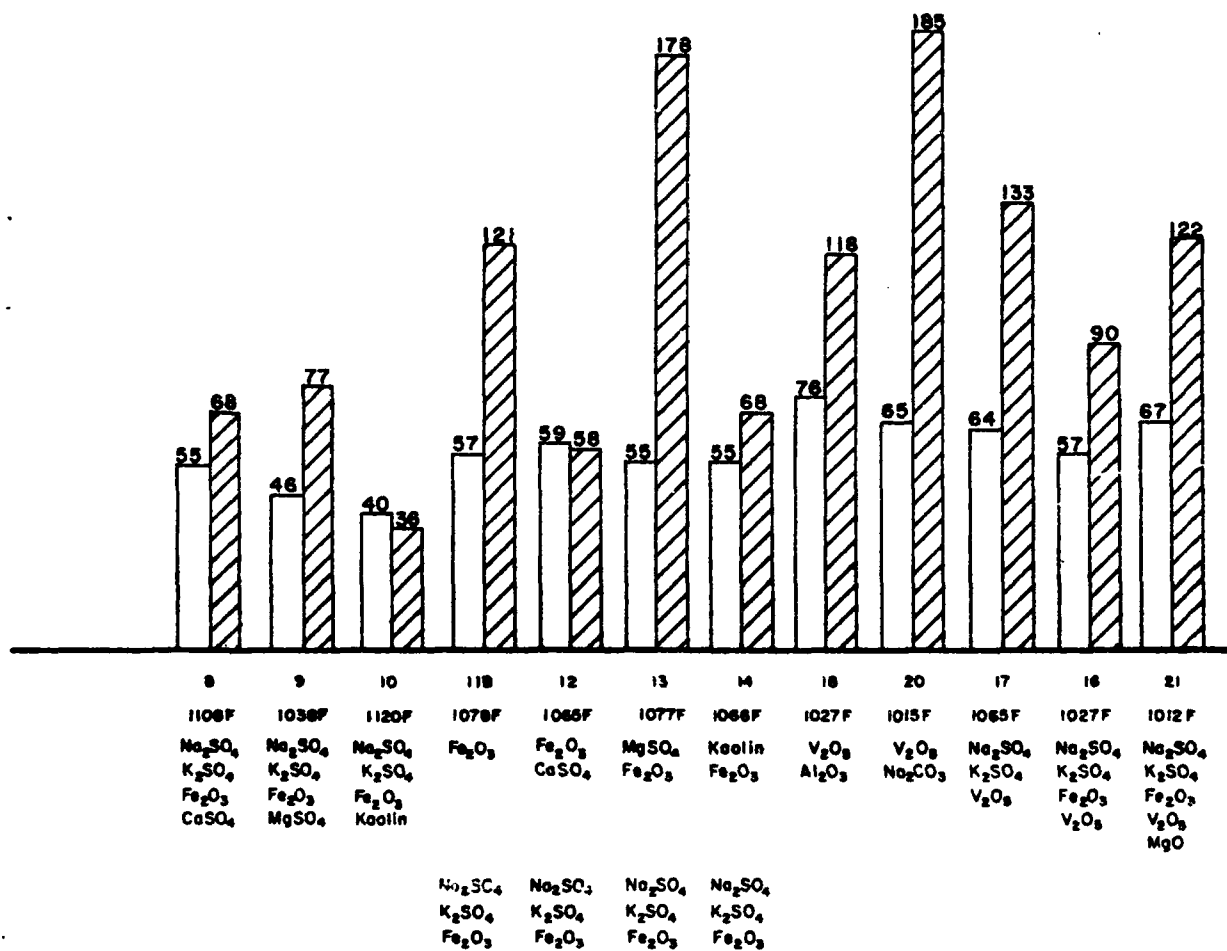
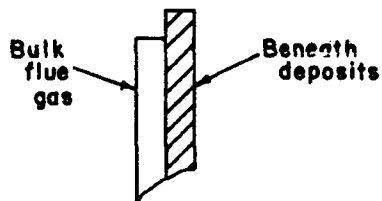
In tests where either Fe_2O_3 was present as the single material in the deposit, or Fe_2O_3 and the alkali sulfates were not intermittently mixed, no hard chunks or fused deposit was observed. Conversely, in each test where Fe_2O_3 was present and mixed with alkalies, at least some hard or fused deposit was observed. The addition of CaCO_3 , CaSO_4 , MgSO_4 , or kaolin did not prevent the formation of hard deposits.

The presence of vanadium definitely led to hard, clinker-like deposits in each test where alkalies were also present, undoubtedly because alkali vanadyl vanadates were formed. Sodium vanadyl vanadate, $5\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 11\text{V}_2\text{O}_5$, melts at 995 F, which was exceeded in these tests. When MgO was present, the formation of hard deposits was limited to the upper $\frac{1}{4}$ inch of the deposit. MgO is known to increase the melting temperature of vanadium-containing deposits. (2,3)

Examination of the deposits at the end of the tests using the index-of-refraction method showed:

Test	Composition by Optical Examination
1	Considerable trisulfates.
6,19	30 to 50 percent trisulfate in white layer.
10	About 5 percent trisulfate in chunky layer.
9	Estimated 2 to 3 percent trisulfate in chunky layer.
7	Estimated 2 to 3 percent trisulfate in chunky layer, with CaCO_3 converted to CaSO_3 and CaSO_4 .
5	About 2 percent trisulfate in chunky layer.
21	About 1 percent trisulfate (an unidentified material also present).
11B	Less than 1 percent trisulfate in hard chunks.
15	Small amount of trisulfate, plus some intermediate compound.
8,13	Trace of trisulfate in chunky or hard layer.
16,17	No trisulfate (an unidentified material present).
2,3A,3B,4 11A,12,14 13,20	No trisulfate detectable.

FIGURE 9. SO₃ CONCENTRATIONS



ABOVE AND BENEATH DEPOSITS

It is difficult to draw firm conclusions from these data, but it is evident that segregation can occur to form distinct white layers, even in periods as short as five hours, and that these layers can be relatively rich in trisulfate (Tests 1, 6, and 19). The high SO_3 concentration measured beneath the deposit in Test 1 is thought to be in error.

Test 4 was anomalous in that no trisulfates were found even though Na_2SO_4 was available and the temperature was 1043 F.

Lack of formation of significant trisulfates in Test 11A may have been a result of the higher temperature as compared to Tests 1, 19, and 6 where appreciable amounts of trisulfates were formed.

The presence of kaolin (Test 10), of MgSO_4 (Tests 9 and 13), of CaSO_4 (Test 8), and of CaCO_3 (Test 7) did not prevent the formation of trisulfates, but the quantity of trisulfate present was small. In Test 7, the CaCO_3 was converted to CaSO_3 and CaSO_4 . Although no trisulfate was found in the deposits from Tests 11A, 12, and 14, it is possible that some slight quantity might have formed although it was masked in the sintered hard layer.

That potassium is more reactive than sodium is suggested by Test 5 where trisulfate was definitely identified, whereas none was found in Test 4.

A deposit consisting of separate layers of Fe_2O_3 and alkali sulfates formed only a small amount of trisulfate at the interfacial layer. This contrasts to the 30 percent or more trisulfate found in local spots when the Fe_2O_3 was intimately mixed with the alkali sulfate.

In the tests with vanadium, appreciable quantities of an unidentified material were present. Lacking any further information, it can be assumed to be sodium vanadyl vanadate because of its low melting point.

CORROSION FROM SULFUR-CONTAINING COMPOUNDS

by

P. D. Miller

The importance of the alkali iron trisulfates in causing superheater corrosion has been stressed by many investigators.⁽⁴⁾ For the past two years, the research at Battelle-Columbus has paid particular attention to the way these compounds are formed and how they participate in the corrosion process. In addition to the trisulfates, the pyrosulfates also can be important in high-temperature corrosion, but their instability as they are heated limits the temperature range over which they can be corrosive. Nevertheless, because of the high chemical activity of the pyrosulfates, several investigators have considered them as a major cause of metal wastage.

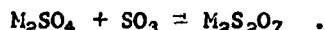
For example, Crossley^(5,6) has repeatedly suggested that the alkali pyrosulfates are the cause of corrosion at temperatures in the range 1000 F to 1200 F and particularly at 1100 F. Nevertheless, X-ray diffraction analyses of the innermost layers of superheater deposits examined by Crossley have failed to show the presence of pyrosulfates. It is argued that this lack of identification may merely be because the pyrosulfates are not present in a suitable crystalline form or in a quantity able to be identified by X-ray diffraction, or because they are so reactive that they have combined further with fly ash constituents such as silicates.

Crossley reported that extensive analyses of deposits showed a ratio of SO_3 to Na_2O and K_2O which would agree with pyrosulfate compositions. Thus by inference it could be argued that pyrosulfates were present at some stage of the corrosion process. He reported further⁽⁷⁾ that experiments showed that pyrosulfates rapidly attacked steel to form ferric oxide and trisulfates at 1110 F.

The corrosion of furnace wall tubes in Germany was attributed by Kirsch⁽⁸⁾ to alkali pyrosulfates. He reported that the fused layer in a deposit melted in the range 930 F to 1470 F, so it would be assumed that the tube surfaces were at these temperatures.

Further support for the importance of pyrosulfates has been presented by Barnhart.⁽⁹⁾ He suggested that potassium pyrosulfate caused the initial attack in high-temperature areas in boilers. He argues that thermodynamic considerations and laboratory studies with pyrosulfates and iron filings indicate reactivity. Potassium pyrosulfate was quite stable according to these studies.

None of the above investigators has presented detailed data supporting the idea of a pyrosulfate mechanism, mainly because of the instability of pyrosulfates at superheater temperatures. A recent paper by Coats and his associates⁽¹⁰⁾ is directed towards a better understanding of this system. This continuing study by the CEBG in England clearly defines the conditions under which molten phases can appear in the K_2SO_4 - Na_2SO_4 - SO_3 systems, in particular with the reaction:



The effect was shown here of temperature and the partial pressure of SO_3 on the formation of liquid phases containing pyrosulfates. Results for the potassium salts are reproduced in Figure 10, including an extrapolation to higher

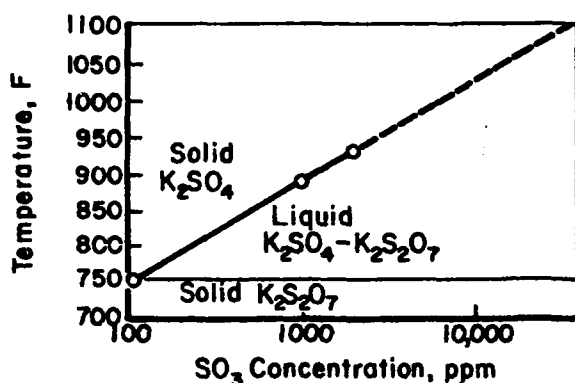


FIGURE 10. EFFECT OF TEMPERATURE AND SO_3 CONCENTRATION ON THE $\text{K}_2\text{SO}_4\text{-K}_2\text{S}_2\text{O}_7$ SYSTEM⁽¹⁰⁾

temperatures. It can be seen that at 1100 F, the SO_3 concentration would need to be very high (about 3.5 percent) to produce conditions where a liquid phase would be present. Even at 1050 F, some 1.5 percent SO_3 would be necessary. Only when the temperature is as low as 900 F is there likely to be enough SO_3 in the layer of gas in contact with the tube surface to insure the formation of a liquid phase, in this case assuming half of the SO_2 in the flue gas were oxidized to SO_3 . This could explain why corrosion reactions occur at metal temperatures below 900 F, as was observed more than 20 years ago with wall tubes. The same arguments fail when the temperature is higher unless some way is explained whereby the sulfur oxides in the gas layer next to the metal surface can be 10 to 20 times greater than in the bulk flue gas.

Under the proper conditions, the SO_3 level can approach that of the SO_2 . Measurements made at Battelle-Columbus using a laboratory probe to study the gas composition near catalytic surfaces indicated that as much as 2000 ppm SO_3 was indeed formed in such areas when the bulk flue gas contained 2800 ppm SO_2 . Thus it is possible that, within porous deposits which are highly catalytic, the conditions can be such that essentially all the SO_2 is converted to SO_3 . In no case, however, can the SO_3 concentration exceed that of the SO_2 . Hence, any pyrosulfates possible at the levels of sulfur oxides found in flue gas should occur only below about 950 F, assuming a maximum SO_3 level of 3000 ppm.

Coats also showed that the potassium salts require much less SO_3 for the formation of liquid phases than do the sodium salts, hence corrosion would be expected to be worse in deposits higher in potassium content. Mixtures of Na_2SO_4 and K_2SO_4 can form liquid phases at temperatures as low as 635 F at SO_3 concentrations as low as 200 ppm, but these conditions obviously are not related to the corrosion of superheater elements.

The question of the importance of the ratio of sodium to potassium has been considered further in a recent paper by Borio and his associates,⁽¹¹⁾ who conducted extensive studies on the corrosiveness of combustion products from coal. They found that the corrosion rate in the range 1000 F to 1150 F increased as the molar ratio of $\text{Na}_2\text{O}/\text{K}_2\text{O}$ in the coal increased, based on acid-soluble portions of the coal. While this work did not attempt to determine the mechanism of the corrosion, the implication was that the complex iron sulfates were involved in the reactions rather than the pyrosulfates.

The case against alkali pyrosulfates in corroding superheater elements or gas turbines is still unclear. But the fact that pyrosulfates have not been positively identified in superheater corrosion areas or in other zones where metal temperature is above 1000 F, and that the SO_3 available even by oxidizing all the SO_2 in flue gas is still insufficient to form pyrosulfates above 900 F, casts considerable doubt on the importance of the pyrosulfates in causing metal wastage. On wall tubes and economizers where metal temperatures are much lower than in superheaters, pyrosulfates can contribute to corrosion. At higher temperatures, they are unlikely to be a cause of trouble.

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WTR/HHK/REB/PDM:ebk

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